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We review and summarize the (sparse) existing scientific and technical literature on the viscosity and elasticity of concentrated fiber suspensions, including reinforced plastics. We also discuss our own experimental capillary rheometry of model suspensions of 1/8" glass fibers in viscous silicone oils. At high volume fraction fibers such suspensions are pseudoplastic, exhibit a yield stress in shear, have large capillary entrance corrections, but show no die swell.

A brief account is given of the influence of fiber breakage on suspension viscosity in capillary flow and on the best choice of technique for mixing such suspensions.

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FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 87, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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The Rheology of Concentrated Suspensions of

Fibers and Spheres

INTRODUCTION

A large portion of short fiber reinforced thermoset and thermoplastic materials are processed by flow molding techniques including transfer molding, injection molding, and compression molding. Each of these processing techniques involves the flow in complex geometries of suspensions of short fibers (usually glass) and/or rigid particles in fluids which are polymer melts or liquid prepolymers. Typically, these suspensions are highly concentrated (10 to 50% solids by volume); and they often contain trace amounts of an immiscible second phase such as water, a lubricant, or a wetting agent.

The rational design of molding equipment including plasticating devices, molding machine runners and gates, and molds requires a knowledge of the flow properties of the material to be molded, at the processing conditions of temperature, pressure, and shear rate. These flow properties are known to depend on material variables such as matrix rheology; fiber length, stiffness, and strength; volume fraction of fibers and/or particulate fillers; and the nature and amount of wetting agents, lubricants or other additives. Naturally, one cannot evaluate the flow properties for every material of potential interest, and one would very much prefer to have sufficient empirical knowledge and theoretical support to be able to predict the flow behavior of commercial molding compounds with some certainty.

In this laboratory we are engaged in developing the requisite empirical background concerning the rheology of concentrated fiber suspensions necessary to construct-

ing a well-founded model of reinforced plastics processing. Most of the data available in this area are confounded by problems with resin and/or fiber degradation, or lack of control of one or more important variables. By carrying out controlled experiments on well characterized systems, we hope to unravel some of the complexity of these technically important materials.

Significance of Rheological Measurements in Concentrated Suspensions

Before discussing the literature on concentrated suspensions, it is well to remember that viscosity is a true material parameter only for homogeneous materials and that short-fiber-reinforced plastics may seldom be treated as homogeneous. As a result, the measured viscosity of a suspension may depend upon both the flow geometry and the geometry of the suspended material. A particula. suspension may have different properties in similar geometries of different size; for example, the viscosity of a suspension in capillary flow may depend upon the diameter of the capillary.

The dependence of viscosity on geometry is due both to the orientation of the fibers during flow and to the interaction of particles with the wall of the measuring instrument. Wall interaction, which has been most thoroughly studied for spheres and dilure suspensions, is described in terms of (a) mechanical interaction involving physical contact of the particle with the wall, (1, 2); b) hydrodynamic interaction in which the presence of the wall alters the velocity profile around the particle, (3, 4) and c) radial migration in which particles in tube flow migrate either toward or away from the flow axis. (5-9).

Although the magnitude of these effects in dilute fiber suspensions does not appear to be large (10), their importance in concentrated suspensions of fibers is unknown. Thus, although summarizing short-fiber-reinforced plastic flow data in

terms of viscosity is useful for interpretation in terms of past experience, it is well to remember that the data may be valid only for the geometry in which it was measured.

Review of Concentrated Suspension Viscosity Data

The flow of concentrated suspensions of spherical particles has been the subject of considerable study for many years (11-13). While classical studies were concerned primarily with the effect of volume fraction of solids on suspension viscosity, more recent studies have considered effects of particle size and particle size distribution (8, 14), wetting and second fluid phases (15-17) and viscoelasticity of the fluid phase (18-23).

A synopsis of experimental literature on the rheology of concentrated fiber suspensions done outside our laboratory is shown in Table 1. The columns of Table 1 are mostly self-explanatory; "force fluctuation" refers to the observation by some researchers that the force required to extrude fiber suspensions through capillaries fluctuates with time. Insufficient data were available to compare the flow curves from all researchers on the same basis, so the qualitative comparison of Fig. 1 was constructed. Only the relative shapes and shear-rate ranges of these curves are significant.

None of these works provide a firm basis for understanding melt-state rheology of reinforced plastics. The thrust of the works of Bell, (29), Takano (31, 32) and Karnis et.al., (33) was to measure the effect of various parameters on fiber orientation in flow; and no quantitative viscosity data were published. The data of Mills (28) is fragmentary, as only two capillary viscosity points for fiber suspensions were published. Carter and Goddard (27) and Ziegel (30) measured suspensions with fiber concentrations well below those of commercial interest. Newman and

TABLE 1. PREVIOUS MEASUREMENTS ON CONCENTRATED SUSPENSIONS OF FIBERS

RESEARCH GROUP	VISCOMETER TYPE	VISCOMETER DIMENSION (in) (dia/gap)	MATRIX MATERIAL	FIBER TYPE	FIBER LENGTH (in)	ASPECT RATIO	VOLUME FRACTION (%)	SHEAR RATE (sec^{-1})	FORCE FLUCTUATION	YIELD STRESS	FIBER BREAKAGE
Stankoi et.al. (24)	Capillary	0.35-0.47	Polyester and Kaolin clay	Glass	0.8	?	15	5-150	YES	YES	NO
Thomas & Hagen (25)	Capillary	0.06	Polypropylene	Glass	0.18 -0.44	?	0-40	0.38 -386	YES	NO	PERHAPS
Newman & Trementozzi (26)	Capillary	0.5	Styrene-Acrylonitrile (co-polymer)	Wollastonite	10^{-3}	10	0-50	3-3000	?	?	?
Carter & Goddard (27)	Cone&Plate	0.16	polybutene oil	Glass	0.008 -0.03	52-228	0.5 -2.2	0.167 -167	?	NO	NO
Mills (28)	Capillary	?	polyethylene	Glass	0.25	400	20	30 & 900	?	YES	YES
Bell (29)	Capillary	0.12-0.25	B-staged epoxy	Glass	0.125	200	45-63	8-100	YES	?	?
Ziegel (30)	Couette	?	Various polymers, liquid at R.T.	Glass	0.24	500	2	0.5 -1.2	?	YES	
Takano (31-32)	Capillary	1"-1/4" Rectangular	B-staged epoxy	Glass	0.125 -0.5	200 -800	0-60	?	YES	YES	YES
Karnis, Goldsmith & Mason (33)	Couette & Capillary	0.076-0.40	Castor oil	Nylon	0.049	8	8	?	No force Measurements		?

Trementozzi (26) were primarily interested in the effects of fillers on die swell. They published one specific viscosity versus fiber concentration curve, although the fibers involved were quite small and had low aspect ratios.

Thomas and Hagen (25) undertook a more thorough study of short-fiber-reinforced thermoplastic rheology with variables in the region of commercial interest for suspensions of glass fibers in polypropylene. Their flow curves fit a power law model, and no yield stresses were observed. Microscopic inspection of the extrudate showed no fiber migration and possible fiber breakage only at the highest shear rates. Their quantitative results, however, are obscured by resin degradation incurred in mixing.

Stankoi, et.al. (24) measured viscosities of suspensions of glass fibers and kaolin clay in a polyester prepolymer. Their flow curves, which displayed yield stresses, were consistent with a Bingham plastic model. They observed no fiber migration and no fiber breakage. Since they did not report matrix resin rheological data, it is difficult to generalize their quantitative data to other systems.

Elastic Effects and Normal Stresses in Concentrated Suspensions

A number of contradictory observations have been made concerning elastic and normal-stress-driven phenomena in fiber suspensions. Newman and Trementozzi (26) found that the addition of Wollastonite filler to a viscoelastic resin greatly reduced the capillary die swell. Carter and Goddard (27) detected no phase lag in dynamic oscillatory testing of a suspension of short fibers in a cone and plate instrument, but they measured large primary normal stress differences. As discussed later, Roberts (34, 35) observed massive Weissenberg rod climbing and very large capillary entrance corrections for a suspension (glass fibers in an inelastic oil) which displayed no die swell and no elastic recovery when rapidly deformed.

Recent Study of Fiber Suspension Rheology

The review above indicates that there is little agreement among researchers about the flow behavior of concentrated fiber suspensions, even on a qualitative level. Their results do suggest, however, the following points:

i) concentrated fiber suspensions are highly non-Newtonian and they may have high yield stresses,

ii) force vs. displacement curves in capillary rheometers show fluctuations, probably due to "log-jamming" at the capillary entry,

iii) flow properties may be sensitive to fiber orientation and, hence, to viscometer geometry,

iv) Brodnyan's theory (36) of fiber suspension rheology predicts viscosities which are orders of magnitude too large for concentrated suspensions of high aspect ratio fibers,

v) fiber breakage during flow can be severe, and

vi) observations of elastic effects are contradictory.

In view of the difficulties inherent in working directly with short-fiber-reinforced plastics, we are studying the rheology of a model system of glass fibers in silicone oil, (34, 35, 37-39). Viscosity measurements are made using the large bore capillary rheometer shown in Fig. 2. This device, which is designed for room temperature operation, allows for the measurement of steady flow viscosity and capillary entrance corrections over the shear rate range of 0.055 to 550 sec.$^{-1}$. A series of 1/4" diameter capillaries are available having length-to-diameter ratios from 1 to 32. A second series of 1/8" diameter capillaries has recently been obtained which will extend the available shear rate range up to about 5500 sec.$^{-1}$.

A typical non-Newtonian viscosity curve obtained with the rheometer for a 15 v/o suspension of 1/8" glass fibers in a 600 poise silicone oil is shown in Fig. 3.

These data have been corrected for capillary entrance losses using the method of Bagley (40). However, they are not corrected for non-Newtonian effects (Rabinowitsch correction), nor have they been corrected for the yield stress which is clearly suggested by a replot of the same data as shear stress vs. shear rate.

We are currently determining the dependence of suspension viscosity on matrix viscosity, fiber length and concentration, shear rate, and rheometer diameter and entry configuration. We are paying special attention to developing a technique for mixing fiber suspensions which avoids fiber damage and air entrapment but ensures fiber dispersion and property reproducibility.

Apanel (37) and Shelton (38) carried out some preliminary studies on the effect of repeated capillary extrusion on the viscosity and fiber length distributions of 15 v/o 1/8" glass fibers in silicone oil. Photomicrographs of a typical suspension taken after various numbers of runs, Fig. 4, clearly show that breakage occurs. Figure 5 shows typical extrusion data. The curves for the 1" and 6" capillaries, when normalized, superimpose to yield one curve, indicating that fiber damage occurs in the capillary entry region and not during passage through the capillary. The extent of damage is higher at higher extrusion rates, but a suspension which showed no measurable degradation after multiple passes at low shear rates showed a considerable drop in viscosity when tested at high rates Fig. (5). From this observation we can conclude that a drop in extrusion force may not be a sufficient test of fiber damage.

Roberts (34, 35) has completed an exploratory study of the viscosity of mixed suspensions of various ratios of 1/8" glass fibers to 30μ glass spheres, at a constant total solids volume fraction of 15% in the 600 poise silicone oil. His viscosity data are shown in Fig. 5 and plots of the "Bagley end correction," e, (40) versus shear

stress are shown in Fig. 7. Even though these end corrections are quite large (usually indicating high elasticity), the suspensions exhibited no die swell upon exiting from the capillary. They do exhibit a very strong Weissenberg rod climbing effect, as shown in Fig. 8.

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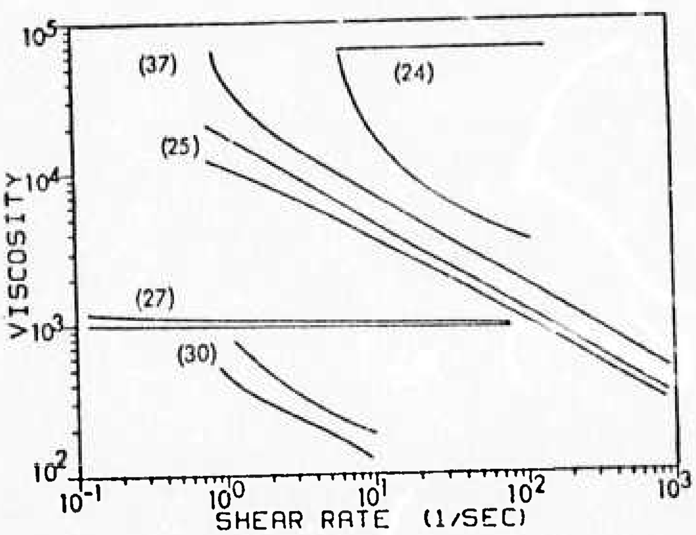


Fig. 1: Qualitative comparison of viscosity data for suspensions of fibers.

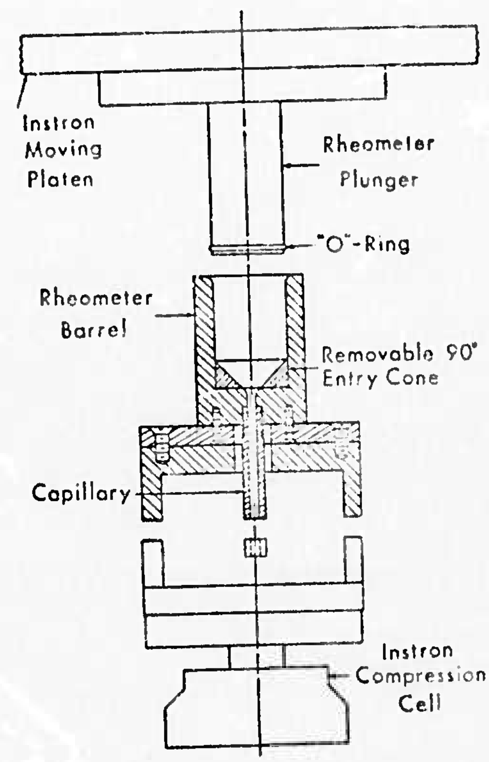


Fig. 2: Capillary viscometer.

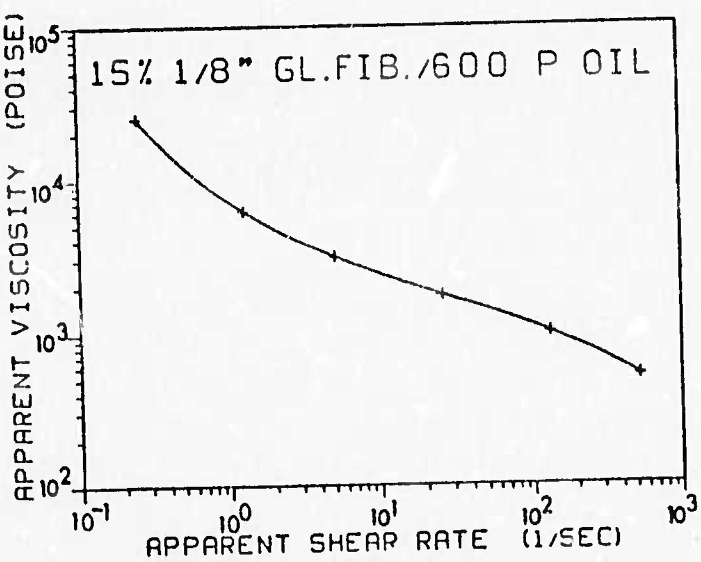


Fig. 3: Viscosity of glass fiber/ silicone oil suspension.

Fig. 4: Photomicrographs of glass fibers after repeated extrusion through the capillary viscometer. Left to right, after zero, ten, and twenty runs. The dark bar is a bundle of fibers 1/8" long. (37)

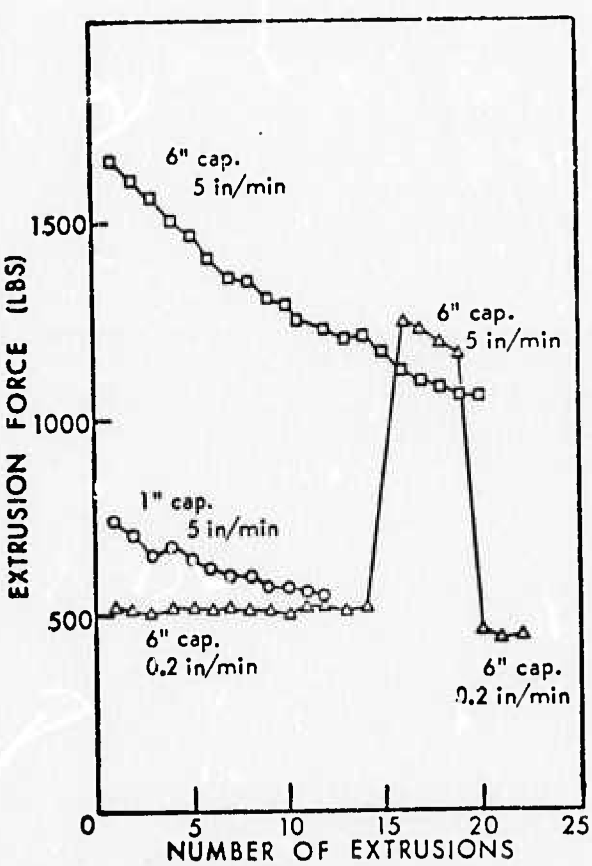


Fig. 5: Effect of repeated extrusion on extrusion force for suspensions of 15v/o glass fibers in silicone oil. Legends indicate capillary length and Instron crosshead speed. (37)

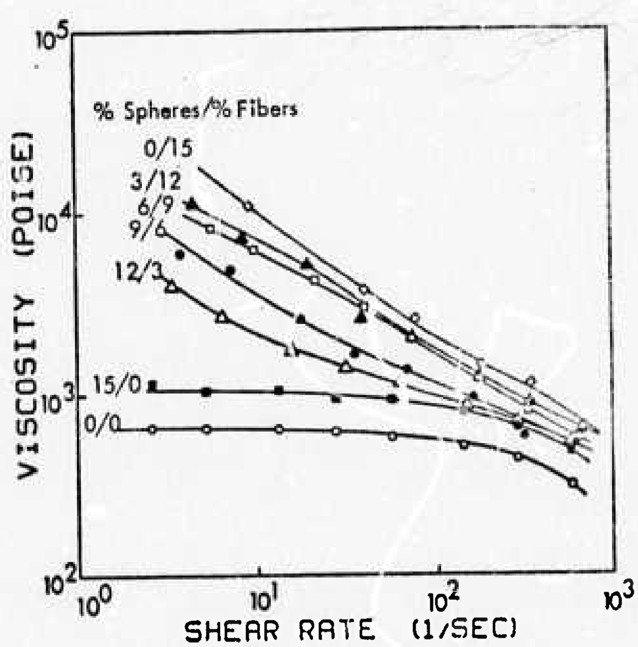
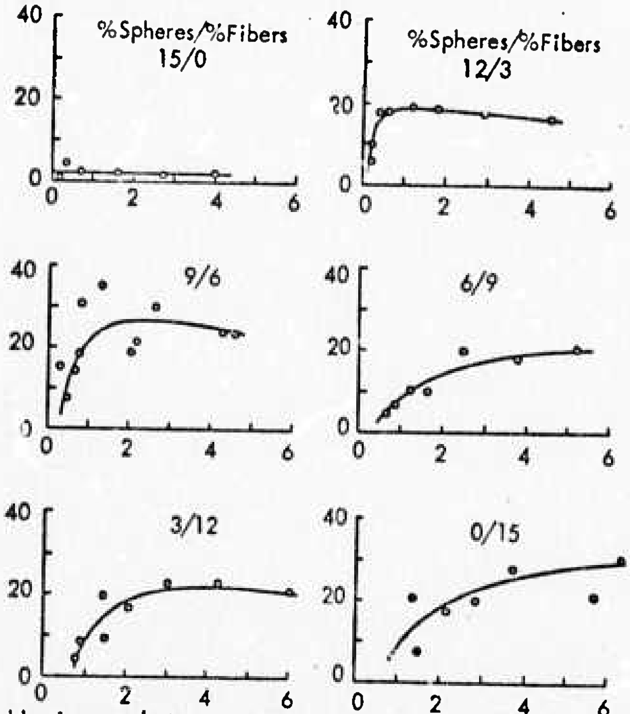


Fig. 6: Viscosities of glass sphere/glass fiber/silicone oil suspensions. (34)



Horizontal Axis: Shear Stress (psi)
Vertical Axis: End correction

Fig. 7: End corrections for glass sphere/ glass fiber/silicone oil suspensions. (34)

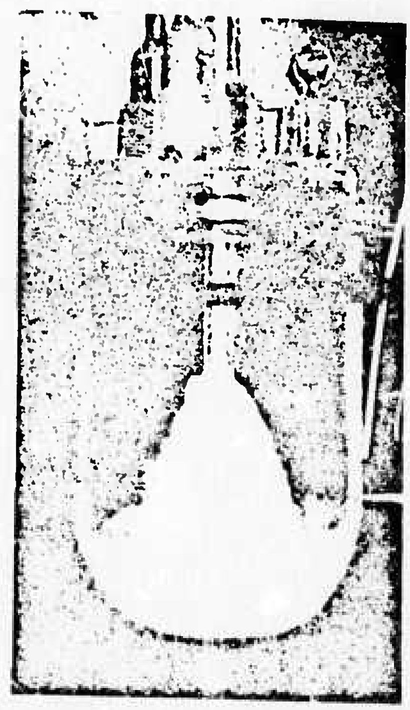


Fig. 8: Rod climbing during mixing of 3 v/o glass fibers, 12 v/o glass beads in silicone oil at 2 rpm. (34)